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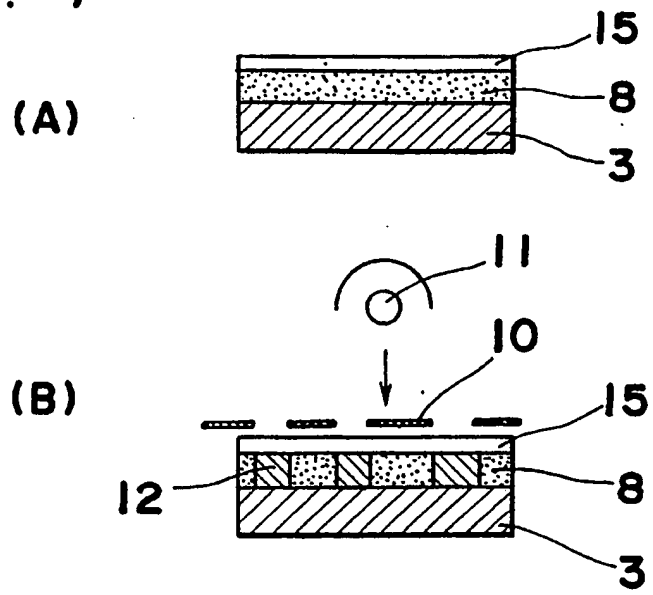
(54) Light transmission paste and metallic copper deposition method using same.

(57) Light transmission paste and a metallic copper deposition method of the present invention can educe the metallic copper in the desired portion by the applying or the contacting of the light transmission paste on the cuprous oxide and the applying of the light upon the desired portion. Also, the light is applied through a mask corresponding to the pattern to be obtained, so that the desired circuit pattern may be easily obtained. Further, the metallic copper of high density may be educed by the contacting or the applying of the metal deposition paste upon the metal of the substrate.

Fig. 1



EP 0 414 140 A2

LIGHT TRANSMISSION PASTE AND METALLIC COPPER DEPOSITION METHOD USING SAME

BACKGROUND OF THE INVENTION

The present invention generally relates to light transmission paste and a metallic copper deposition method using it.

A circuit pattern formation in the conventional hybrid IC was effected by a printing method on an alumina ceramic substrate. The fundamental component in the printing method Is composed of a screen 1 which has an empty hole corresponding to the circuit pattern to be drawn on the substrate and a squeegee 2 as described in Fig. 5. Also, the screen 1 is retained in parallel to the substrate 3 and in a position of approximately 0.25mm through 2.0mm of the surface of the substrate 3. Conductive paste 4 which becomes patterns 5 is placed on the screen 1. The conductive paste 4 is depressed by the squeegee 2 moving while depressing the screen 1, and is moved together. As a result, the conductive paste 4 is moved onto the substrate 3 from the empty hole portion in the screen 1, and the pattern 5 are formed on the substrate 3.

It is proposed recently that the patterns should be formed on the substrate by a drawing method. The conductive paste 4 is filled into a paste cartridge 7. The paste cartridge 7 is formed cylindrical, is contracted in its lower end portion, and is provided with an empty hole of 0.06 through 2mm in diameter. The paste which is in the cartridge having a certain diameter hole at lower end portion by the pressure application through the air or the like upon the upper end portion of the paste cartridge 7. By the movement of the paste cartridge 7 while the paste discharging is getting performed, the pattern 5 of a given line width is be drawn.

In the printing method, the screen 1 is necessary to be exchanged when the pattern to be obtained has been exchanged. The screen 1 is expanded through a certain number of printing operations if the pattern is the same. Thus, the positional shift is caused in the printed pattern 5. Therefore, the screen is required to be exchanged on the way. The uniform screen 1 is not always available, when the screen is necessary to be exchanged, because of the working accuracy of the screen frame, the accuracy necessary when the screen 1 is pasted on the frame, and so on. Therefore, in the exchange of the screen 1, the adjustments such as new positional alignment, parallel arrangement of the substrate 3 and the screen 1 are necessary. But it takes about thirty minutes at least for the adjustment, thus reducing the operation rate of the hybrid IC production line.

When the pattern 5 is designed, and tested, about four days are required to make the screen, so that the development period is caused to be extended.

In the drawing method, a program with pattern coordinates having been inputted has only to be changed even in the changes of the pattern 5, so that these causes hardly stop the hybrid IC production line. But the empty hole in the tip end portion of the paste cartridge 7 at this time is restricted to 0.06 through 2mm in diameter, also is basically pattern formed with the lines, with a disadvantage that the productivity is extremely lower as compared with the printing.

Recently a method of making a pattern forming circuit which is not reduced in the operation rate of the hybrid IC production line even in a case where the substrate different in the pattern is obtained, and further is available even in the mass production. In one example, the disproportioned reaction of cuprous oxide is used.

The reaction expressed by

$$2Cu^{+} \rightleftarrows + Cu^{o} + Cu^{2+} \quad (1)$$

is caused in a portion where the light of 280nm through 640nm has been applied under the weak acidic atmosphere such as 0.002N sulfic acid aqueous solution so as to produce metallic copper, so that the metallic copper may be selectively educed and the pattern is formed.

In order to cause the disproportioned reaction of the cuprous oxide, a document shows that the light of 280nm through 640nm is required to be applied under the weak acidic atmosphere. As shown in Fig. 7 (A), the cuprous oxide 8 was applied on the substrate 3 forming the pattern. Then, as shown in Fig. 7 (B), it was dipped into the weak acidic aqueous solution such as dilute sulfuric acid or the like. The light of the light source 11 is applied upon it into the pattern by the mask 10, thus obtaining the pattern 12.

But the half of the cuprous oxide applied as shown in the (1) equation became the metallic copper in the disproportioned reaction of the cuprous oxide. It was difficult to raise the ratio. The reduction in the exiting density of the metallic copper caused the electronic circuit having an extremely high resistance value. Therefore, it is necessary to raise the density of the metallic copper by the other method. One of the methods to be generally taken at this time is a physical development. As shown in Fig. 8 (A), the cuprous oxide which was not reacted with aqueous solution sodium thiosulfate or the like was removed. The pattern 12 existing on the substrate 3 was retained in the metallic salt aqueous solution 13 in the reducing atmosphere as shown in Fig. 8 (B) so as to grow around the metallic copper the component

metal of the metallic salt with the metallic copper as a nucleus, thus producing the copper pattern 14 of high density.

In the disproportioned reaction of the cuprous oxide under the weak acidic aqueous solution by this method, the thickness of the weak acidic aqueous solution on it is required to be constant across the whole face with the cuprous oxide existing on it if the precise pattern is intended to form, because the refractive index of the light in the air and within the weak acidic aqueous solution is different. Therefore, the light cannot be applied upon the cuprous oxide until the cuprous oxide put into the weak acidic aqueous solution becomes certain on the weak acidic aqueous solution surface. Thus, it was considerably difficult to use this method for the making of the pattern. Since the acidic aqueous solution caused the corrosion in the contact of the metal, it was difficult to use it in the production line.

In the physical development using the metallic salt aqueous solution within the production line, the problems such as metallic salt aqueous solution exchange, waste processing and so on are undesirably caused.

SUMMARY OF THE INVENTION

Accordingly, an essential object of the present invention is to provide the light transmission paste for deposition the metallic copper by the disproportioned reaction of cuprous oxide except for liquid phase, and a metallic copper deposition method using it.

In accomplishing the object, according to one preferred embodiment of the present invention, there is provided the light transmission paste which includes acidic material and is transparent with the wavelength of 280nm through 640nm.

The present invention is the light transmission paste which includes hydrochloric acid, nitric acid, sulfuric acid or p-toluene sulfonic acid.

The present invention is a metallic copper deposition method, which comprises the steps of applying upon the cuprous oxide provided on the substrate the light transmission paste that includes the acidic material, and is transparent with the wavelength of 280nm through 640nm, thereafter applying the light of 280nm through 640nm upon the desired portion, then removing the light transmission paste, deposition the metallic copper from the cuprous oxide of the irradiation portion.

The present invention is a circuit pattern forming method, which comprises the steps of applying upon the cuprous oxide provided on the substrate the light transmission paste that includes the acidic material, and is transparent with the wavelength of 280rm through 640nm, thereafter applying the light of 280nm through 640nm through a mask having an opening portion corresponding to a pattern to be formed to educe the metallic copper on the irradiation portion, then removing the light transmission paste and the mask, forming the desired circuit pattern on the substrate.

Also, the present invention is a light transmission sheet so composed that the light transmission paste which includes the acidic material, and is transparent with the wavelength of 280nm through 640nm is applied upon the support member which is transparent with the wavelength of 280nm through 640nm.

Also, the present invention is a metallic copper deposition method, which comprises the steps of causing the light transmission sheet of the present invention to contact the cuprous oxide formed on the substrate, applying the wavelength of 280nm through 640nm upon the desired portion of the cuprous oxide from the transparent support member side, thereafter removing the above described light transmission sheet, deposition the metallic copper from the cuprous oxide of the irradiation portion.

Also, the present invention is a circuit pattern forming method, which comprises the steps of causing the light transmission sheet of the present invention to contact the cuprous oxide formed on the substrate, applying the wavelength of 280nm through 640nm upon the cuprous oxide from the transparent support member side through a mask having an opening portion corresponding to a pattern to be formed to educe the metallic copper on the irradiation portion, then removing the above described light transmission paste and the above described mask, forming the desired circuit pattern on the substrate.

Also, the present invention is a metal deposition method, which comprises the steps of causing the metal deposition paste that includes the metallic salt with a metal to be educed provided therein and a reducing agent for reducing, cracking the metallic salt is caused to contact the metal provided on the substrate, deposition the metal of the metallic salt in the above described metallic deposition paste on the metallic surface on the above described substrate.

Further, the present invention is a metallic copper deposition method, by the use of the metallic copper deposition method of the present invention, which comprises the steps of deposition the metallic copper, thereafter causing the metal deposition paste that includes the metallic salt including copper and the reducing agent for reducing, cracking the metallic salt, to contact the copper provided on the substrate,

The light transmission paste of the present invention captures Cu^{2+} of the cuprous oxide upon

which the light of the wavelength of 280nm through 640nm has been applied.

The light transmission paste of the present invention is applied on the cuprous oxide and is caused to come into contact with it, educes the metallic copper on the irradiation portion by the application of the light upon the desired portion.

Also, the metallic deposition paste is brought into contact with the metal on the substrate, so that the metallic copper of high density may be provided.

BRIEF DESCRIPTION OF THE DRAWINGS:

These and other objects and features of the present invention will become apparent from the following description taken in conjunction with the preferred embodiment thereof with reference to the accompanying drawings, in which;

Fig. 1 is a step sectional view showing a circuit pattern forming method in a first embodiment of the present invention;

Fig. 2 is a step sectional view showing a circuit pattern forming method in a second embodiment of the present invention;

Fig. 3 is a step sectional view showing a metallic copper deposition method in a third embodiment of the present invention;

Fig. 4 is a step sectional view showing a circuit pattern forming method in a fourth embodiment of the present invention;

Fig. 5 through Fig. 7 are step sectional views showing the conventional circuit pattern forming method; and

Fig. 8 is a step sectional view showing the conventional metallic copper deposition method.

Embodiment:

Before the description of the present invention proceeds, it is to be noted that like parts are designated by like reference numerals throughout the accompanying drawings.

Embodiment 1

Fig. 1 (A), (B) are sectional views showing a circuit pattern forming method in a first embodiment of the present invention. First, gelatin powder 50g is added into water 500ml. It is heated at 50°C. 36N-sulfuric acid 0.01ml is mixed with the gelatin powder completely melted into the light transmission paste. It is applied on the cuprous oxide 8 applied on the substrate 3 in a dark room. It is cooled, hardened at 5°C into the light transmission membrane 15. This is applied only in the portion for deposition the metallic copper through a stainless-make mask 10 having an empty hole corresponding to the pattern which is adapted to obtain the light of the light source 11 using a tungsten light as shown in Fig. 1 (B). As a result, the light applied through the mask 10 reaches the cuprous oxide through the light transmission membrane 15. At this time, since the cuprous oxide is put under the acidic atmosphere by the light transmission membrane 15, the disproportioned reaction is caused to educe the metallic copper pattern 12. Finally, the light transmission paste 15 was removed. Since the light was not applied upon the aqueous solution sodium thiosulfate (sodium thiosulfate 25g with respect to water 100ml), the disproportioned reaction was not caused. The residual cuprous oxide was removed.

Although the stainless-make mask 10 was used for patterning the light in the present embodiment, the light may be stopped into the beam state and be scanned.

Although the gelatine was mixed into the light transmission membrane 15, the other high molecular agent such as polyvinyl alcohol, cellulose acetate or the like may be used. Further, acidic reagent such as hydrogen acid, sulfuric acid, acetic acid, p - toluene sulfonic acid or the like may be used, instead of the sulfuric acid.

Embodiment 2

Fig. 2 (A), (B), (C) are sectional views showing a circuit pattern forming method in a second embodiment of the present invention. First, gelatin powder 30g is added into water 500ml. It is heated at 50°C. 36N-sulfuric acid 0.01ml is mixed with the gelatin powder completely melted. It is applied as a medicine layer 17 on a transparent support member made of cellulose triacetate as shown in Fig. 2 (A), and the light transmission sheet 18 is made. As shown in Fig. 2 (B), it is caused into contact with the cuprous oxide 8 with the medicine layer 17 of the light transmission sheet 18 being applied on the substrate 3. This is irradiated only upon the portion for patterning, and deposition the metallic copper through a stainless-make mask 10 corresponding to the pattern which is adapted to obtain the light of the light source 11 using a tungsten lamp as shown in Fig. 2 (C). Thus, the light patterned by the mask 10 reaches the cuprous oxide 8 through the transparent support member of the light transmission sheet and the medicine layer 17. At this time, as the cuprous oxide 8 is put under the acidic atmosphere by the medicine layer 17, the disproportioned reaction is caused, and the metallic copper pattern 12 is educed. Finally the

light transmission sheet 18 is removed.

Although the stainless-make mask 16 was used for patterning the light in the present embodiment, the light may be stopped into the beam state and be scanned.

Although the gelatine was mixed into the medicine layer 17, the other high molecular agent such as polyvinyl alcohol, cellulose acetate or the like may be used. Also, although the cellulose triacetate was used as the transparent support member, polyester or the like which is transparent may be used in at least one portion of the 280nm through 640nm. Further, acidic reagent such as hydrogen acid, sulfuric acid, acetic acid, p - toluene sulfonic acid or the like may be used, instead of the sulfuric acid.

Embodiment 3

Fig. 3 (A), (B) show the sectional views showing a metallic copper deposition method in a third embodiment of the present invention. Also, the present embodiment was all carried out in a dark room.

First, gelatin powder 30g is added to water 300ml. It is heated at 50°C and is melted completely. Thereafter, hydroquinone 1g, citric acid 0.6g, copper sulfate 1g are added to it to obtain metallic deposition paste 19. Thereafter, the metal deposition paste 19 is applied on the metal 21 provided on the substrate 3 with the use of a nozzle so as to be retained for five minutes as shown in Fig. 3 (A). Thus, the copper 22 of the copper sulfate to be contained in the metal deposition paste 19 is accumulated on the metal 21 as shown in Fig. 3 (B). Finally the metal deposition paste 19 is removed.

Although the gelatin was mixed in the metal deposition paste 19 in the present embodiment, the other high molecular agent such as polyvinyl alcohol, cellulose acetate or the like may be used. Also, although the acidic hydroquinone was used as the reduction component, the other reduction agent such as α - naphthol or the like. Further, although the copper sulfate was used as a material for supplying the metal, inorganic metallic salt shown by a general equation MnXm (n is 1 or more, M is 1 or more, M is Cn, Zn, Ni, Fe, Ag, Au or the like, X is Cl, Br, I, CN, SO_4 or the like) or organometallic compound shown by (RCOO) mMn (n is 1 or more, m is 1 or more, R is alkyl group, acyl group or the like, M is Cu, Zn, Ni, Fe, Ag, Au or the like) may be used. Also, in the present embodiment, the nozzle was used in the applying of the metal deposition paste, the other applying method such as printing or the like may be used.

Also, a skill of causing the medicine agent in paste state to be previously kept in sheet state for the contacting operation may be used.

Embodiment 4

Fig. 4 (A) through (F) are sectional views showing a circuit pattern forming method in a fourth embodiment of the present invention. First, gelatin powder 50g is added into water 500ml. It is heated at 50°C. 36N-sulfuric acid 0.01ml is mixed with the completely melted gelatin powder into the light transmission paste. It is applied on the cuprous oxide 8 applied on the substrate 3 in a dark room as shown in Fig. 4 (A). And it is cooled, hardened at 5°C into the light transmission membrane 15. This is irradiated only upon the portion for patterning, and deposition the metallic copper through a stainless-make mask 10 corresponding to the pattern which is adapted to obtain the light of the light source 11 using a tungsten lamp as shown in Fig. 4 (B). Thus, the light patterned by the mask 10 reaches the cuprous oxide through the light transmission membrane 15. At this time, since the cuprous oxide 8 is put under the acidic atmosphere by the light transmission membrane 15, the disproportioned reaction is caused, and the metallic copper pattern 12 is educed.

Thereafter, the light transmission membrane 15 is peeled off. Since the light is not irradiated because of aqueous solution sodium thiosulfate (sodium thiosulfate 25g with respect to water 100ml), the disproportioned reaction is not caused. As a result, the residual cuprous oxide is removed. Thus, only the metallic copper pattern 12 exists on the substrate 3 as shown in Fig. 4 (C).

Then, in order to further improve the conductivity of the metallic copper pattern 12 obtained, the metal deposition paste is used. First, gelatin powder 30g is added to water 300ml. It is heated at 50°C and is melted completely. Thereafter, hydroquinone 1g, citric acid 0.6g, copper sulfate 1g are added to it to obtain the metallic deposition paste 19. It is applied on the metallic copper pattern 12 formed on the substrate 3 with the use of a nozzle so as to be retained for five minutes as shown in Fig. 4 (D). As a result, the copper of the copper sulfate is educed on the metallic copper pattern 12 as shown in Fig. 4 (E). Then, these are cooled, hardened at 5°C. The metal deposition paste 19 is removed, so that the metallic copper pattern 14 of high density may be formed on the substrate 3 shown in Fig. 4 (F).

Although the stainless-make mask 10 was used for patterning the light in the present embodiment, the light may be stopped into the beam state and be scanned.

Although the gelatine was mixed into the light

transmission paste, the other high molecular agent such as polyvinyl alcohol, cellulose acetate or the like may be used. Further, acidic reagent such as hydrogen acid, sulfuric acid, acetic acid, p - toluene sulfonic acid or the like may be used instead of the sulfuric acid. Further, the light transmission sheet by the third invention may be used without the use of the light transmission paste.

Although the gelatin was mixed into the metal deposition paste, the other high molecular agent such as cellulose acetate or the like may be used. Also, although the acidic hydroquinone was used as the reduction component, the other reduction agent such as α - naphthol or the like may be used. Further, although the copper sulfate was used as a metal containing component to be used for metal deposition, metallic salt shown by a general equation CuX or CuX_2 (X is Cl, Br, 1, CN, SO_4 or the like) or organic acid metallic salt shown by $(RCOO)_2Cu$ or RCOOCu (R is alkyl group, acyl group or the like). Also, in the present embodiment, the nozzle was used in the applying of the metal deposition paste, the other applying method such as printing or the like may be used.

Also, a skill of causing the medicine in paste state to be previously kept in sheet state for the contacting operation may be used.

As is clear from the foregoing description, according to the arrangement of the present invention, the present invention can educe the metallic copper in the desired portion by the applying or the contacting of the light transmission paste on the cuprous oxide and the applying of the light upon the desired portion.

Also, the light is applied through a mask corresponding to the pattern to be obtained, so that the desired circuit pattern may be easily obtained.

Further, the metallic copper of high density may be educed by the contacting or the applying of the metal deposition paste upon the metal of the substrate.

Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be noted here that various changes and modification will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modification depart from the scope of the present invention, they should be construed as included therein.

Claims

(1) Light transmission paste which includes an acidic material and is transparent with the wavelength of 280nm through 640nm.

(2) Light transmission paste as defined in claim 1, wherein the acidic material is hydrochloric acid, nitric acid, sulfuric acid or p-toluene sulfonic acid.

(3) A metallic copper deposition method comprising the steps of applying the light transmission paste upon cuprous oxide provided on the substrate, thereafter applying the light of 280nm through 640nm upon the desired portion, then removing the light transmission paste, and deposition the metallic copper from the cuprous oxide of the irradiation portion.

(4) A circuit pattern forming method comprising the steps of applying the light transmission paste upon the cuprous oxide formed on the substrate, thereafter applying the light of 280nm through 640nm through a mask having an opening portion corresponding to a pattern to be formed so as to educe the metallic copper on the irradiation portion, then removing the light transmission paste and the mask, and forming the desired circuit pattern on the substrate.

(5) A light transmission sheet, as defined in claim 1, wherein light transmission paste is applied upon a support member which is transparent with the wavelength of 280nm through 640nm.

(6) A metallic copper deposition method comprising the steps of causing the light transmission sheet to contact the cuprous oxide formed on the substrate, applying the wavelength of 280nm through 640nm upon the desired portion of the cuprous oxide from the transparent support member side, thereafter removing the above described light transmission sheet, and deposition the metallic copper from the cuprous oxide of the irradiation portion.

(7) A circuit pattern forming method comprising the steps of causing the light transmission sheet to contact the cuprous oxide formed on the substrate, applying the wavelength of 280nm through 640nm upon the cuprous oxide from the transparent support side through a mask having an opening portion corresponding to a pattern to be formed so as to educe the metallic copper on the irradiation portion, then removing the above described light transmission paste and the above described mask, forming the desired circuit pattern on the substrate.

(8) A metal deposition method comprising the steps of causing the metal deposition paste, which includes metallic salt including a deposition metal and a reducing agent for reducing, cracking the metallic salt, to contact the metal provided on the substrate, deposition the metal of the metallic salt in the above described metallic deposition paste on the metallic surface on the above described substrate.

(9) A metallic copper deposition method as defined claim 3 or 6, further comprising the steps of deposition the metallic copper, thereafter causing the metal deposition paste, which includes metallic salt including copper and a reducing agent for reduc-

ing, cracking the metallic salt, to contact the copper on the substrate, deposition the copper.

Fig. 1

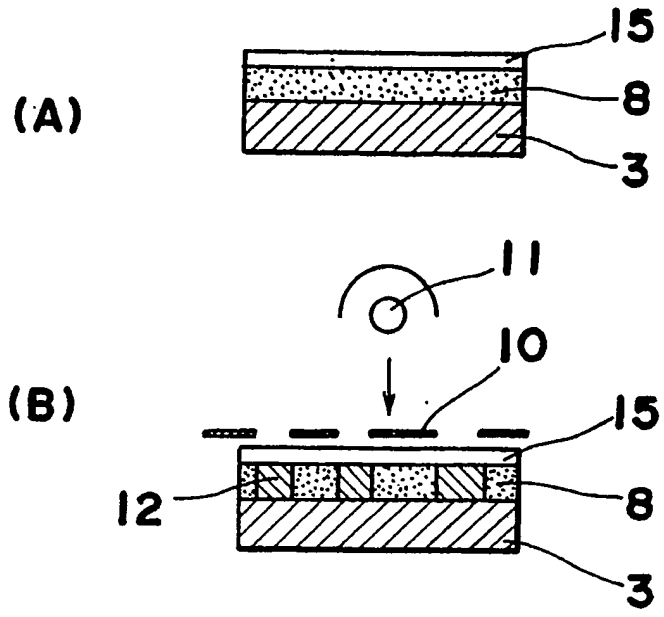


Fig. 2

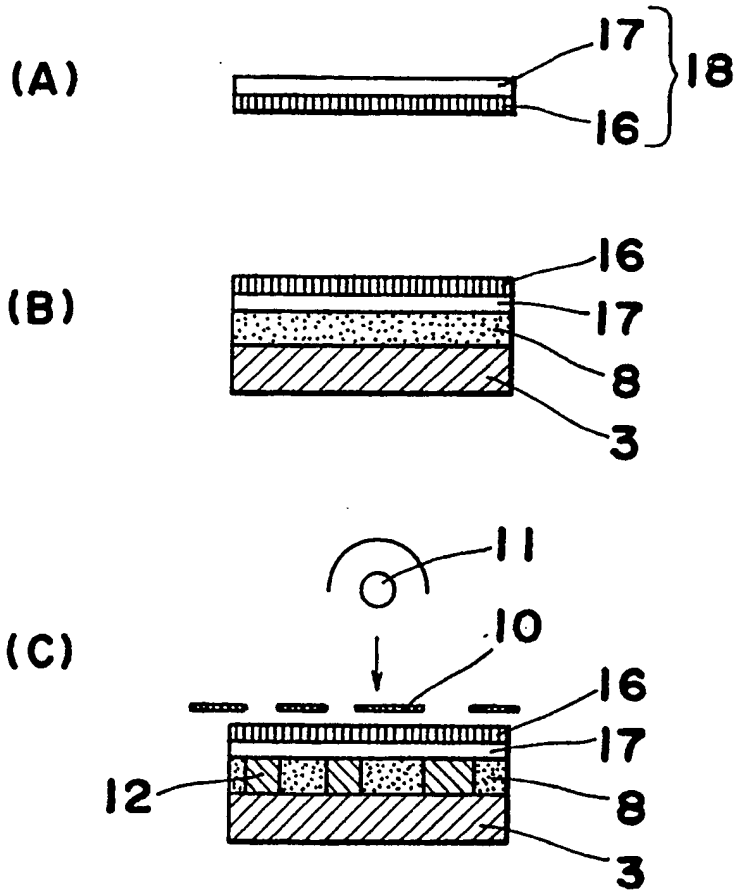


Fig. 3

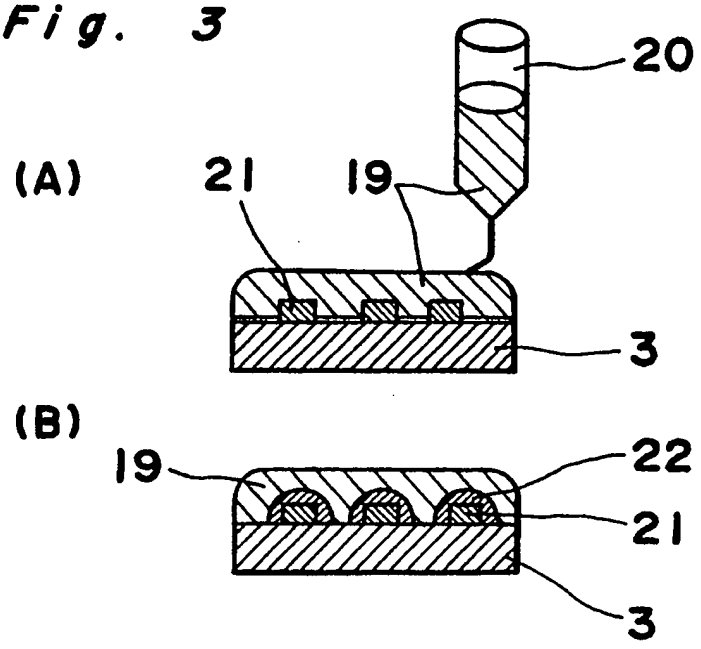
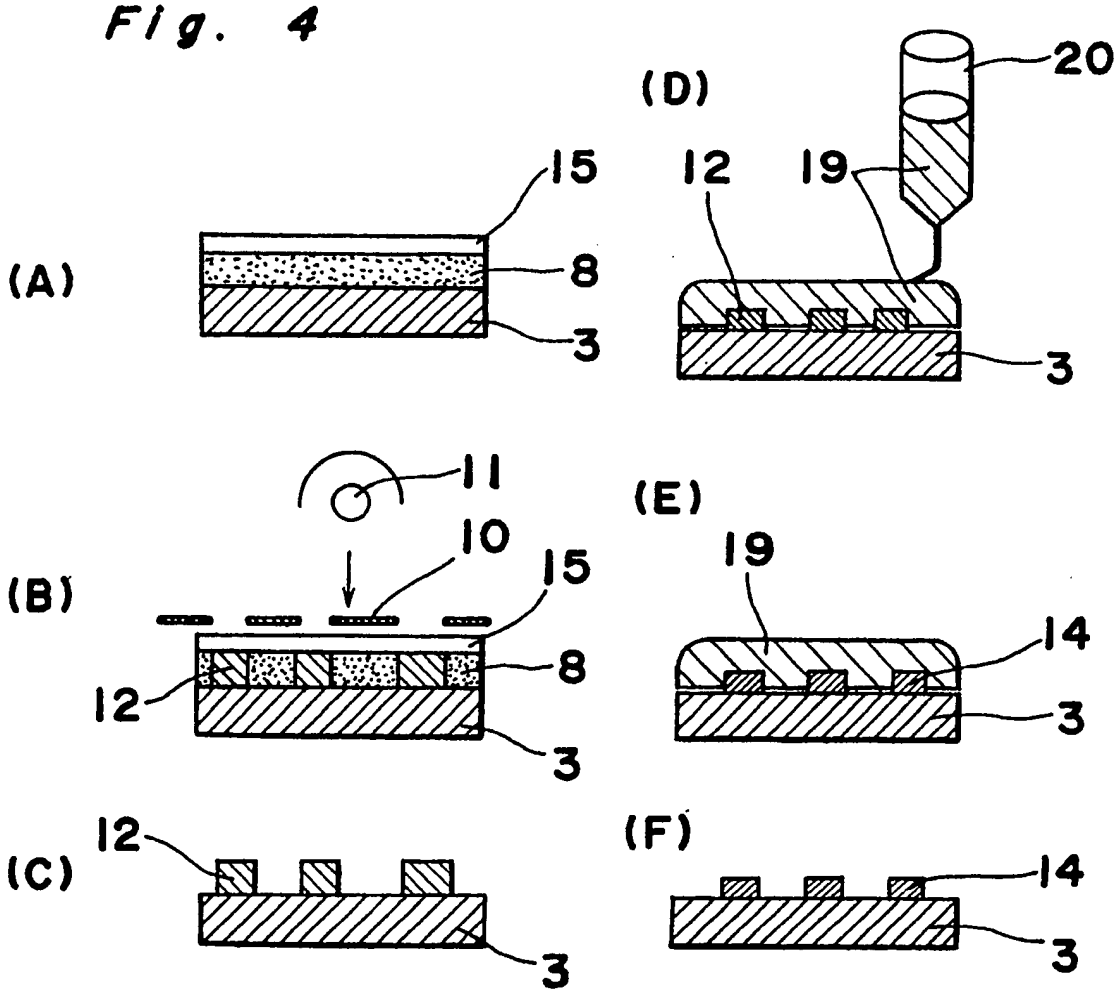

20
(A)
21
19
3
(B)
19
22
21
3

Fig. 4


(D)
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12
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(A)
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3
11
(E)
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(B)
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3
12
(F)
(C)
14
3
3

Fig. 5

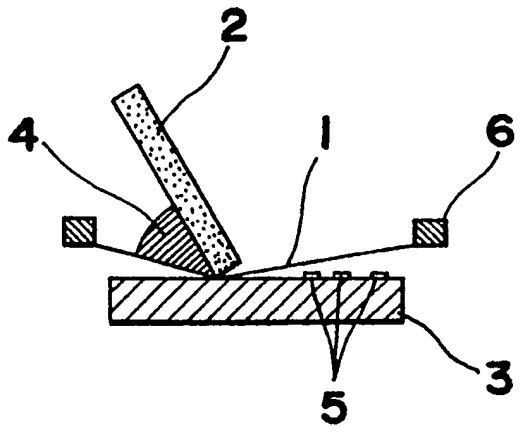


Fig. 6

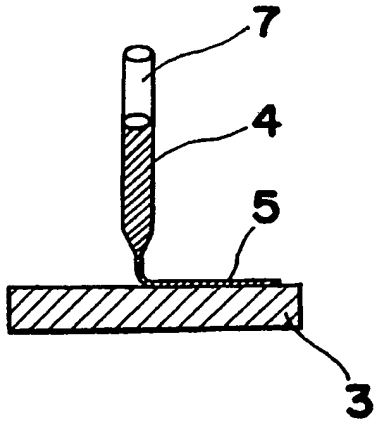
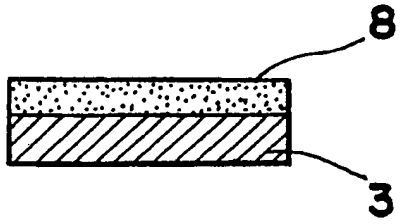


Fig. 7

(A)



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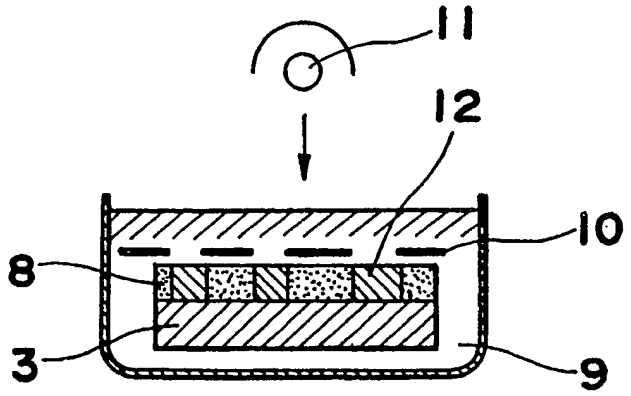
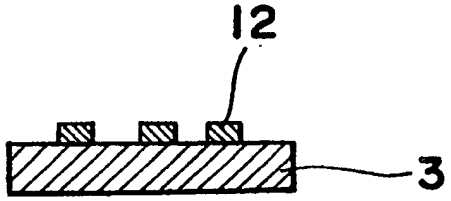


Fig. 8

(A)



(B)

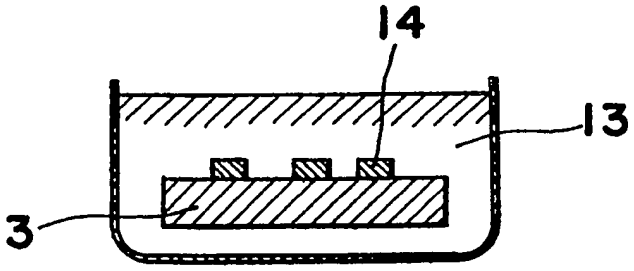


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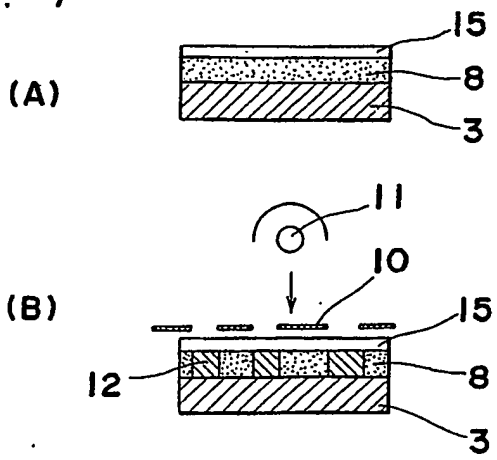
Fig. 1



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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-3 671 249 (T.E.FLYNN) * column 2, lines 14 - 16 * * column 3, lines 5 - 11 @ column 4, lines 23 - 27 @ column 3, line 70 - column 4, line 20 *	1,3,4,7,8, 9	H 01 L 21/48 H 05 K 3/10 C 23 C 18/14 G 03 C 1/725
A	US-A-3 451 813 (L.C.KINNEY ET AL.) * column 1, lines 15 - 29 * * column 4, lines 21 - 44 *	3,4,8,9	
A	US-A-3 056 881 (H.J.SCHWARZ) * claim 6 *	3,4	
A	US-A-3 928 670 (C.R.BRUMMET ET AL.) * abstract *	8,9	
E	EP-A-0 402 966 (MATSUSHITA ELECTRIC WORKS, LTD.) * page 3, lines 11 - 26 * * page 10, lines 38 - 47 *	3,4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H 01 L
H 05 K
C 23 C
G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	05 July 91	ZOLLFRANK G.O.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

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